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TITLE: Positive electrode for rechargeable battery cell - comprises acetylene black, gamma manganese oxide and a **proton conductor**

Michel Jacques
INVENTOR: FORESTIER, M; GUITTON, J ; KAHIL, H

PATENT-ASSIGNEE: CNRS CENT NAT RECH SCI[CNRS]

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ABSTRACTED-PUB-NO: FR 2547678A

BASIC-ABSTRACT:

Electrode comprises a combination of a positive mass (14) of chemically inert electronically conducting material, such as acetylene black; a **mixed conductor of electrons and protons,** such as gamma-MnO and a solid **proton**-conducting mineral or organic body; with an electrolyte consisting of a layer (12) of the above solid **proton** conducting body alone, the two layers being held in a mass together by the effect of pressure.

The **proton conductor** consists of one of the following mineral acids (a) HVO2XO4.nH2O where X is P, As, etc.; (b) HMO3.nH2O where M is Sb, Nb, Ta, etc.; (c) H3(XM12040.30H2O) where X is P, As, etc. and M is Mo, W, etc.

USE/ADVANTAGE - The electrode is for use in a cell or accumulator. The cell has much greater lifetime than the Leclanche cell. It is rechargeable and does not suffer from intermittent discharge. It does not require rest periods.

CHOSEN-DRAWING: Dwg.1/8

TITLE-TERMS: POSITIVE ELECTRODE RECHARGE BATTERY CELL COMPRISE ACETYLENE BLACK GAMMA MANGANESE OXIDE **PROTON CONDUCTOR**

DERWENT-CLASS: L03 X16

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New positive electrode for a rechargeable electrochemical generator and process for its manufacture

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Inventor:	GUITTON JACQUES; FORESTIER MICHEL; KAHIL HASSAN
Applicant:	CENTRE NAT RECH SCIENT (FR)
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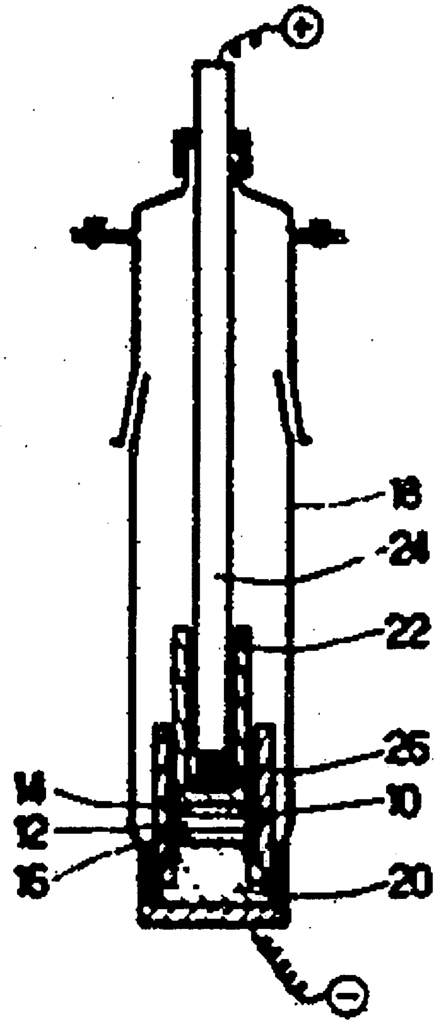
Abstract of **FR2547678**

The electrode is characterised by the combination, on the one hand, of a positive mass 14 consisting of a noncorridable electron-conductive material such as acetylene black, a mixed electron- and proton-conductive material such as manganese oxide MnO_2 of gamma variety, and of an inorganic or organic proton-conductive solid body and, on the other hand, of an electrolyte consisting of a layer 12 of the said proton-conductive solid body by itself, the said two layers being solidified together under the effect of pressure. Application especially to the manufacture of batteries.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Result Page

New positive electrode for generator <RTI ID=1.1> electrochirnic< refillable> /RTI and its manufactoring process .

The present invention relates to an electrode intended to be used like positive electrode of pile or accumulator.

1 It is known that the positive mass of the Leclanché piles to saline aqueous electrolyte is consisted a pulverulent solid mass including/understanding a mixture <RTI ID=1.2> of< a /RTI> variety of manganese oxide indicated by <RTI ID=1.3> Mno 2 there< /RTI> and of black <RTI ID=1.4> dtacetylene.</RTI> the electrolyte is consisted an aqueous chloride solution <RTI ID=1.5> dtammonium.</RTI>

2 <RTI ID=1.6> MnO 2 there< /RTI> is known to be an acceptor of protons. Indeed, so that MnO2 is reduced to cathode, it is necessary that it collects an electron according to reaction EMI1.1 but since it is solid and that it must have a neutral total load, he must collect a proton <RTI ID=1.7> H< /RTI> It was usual to write the total reaction as follows: EMI1.2 but this reaction does not correspond to reality.

<RTI ID=1.8> the correct reaction s1 writes< /RTI> EMI1.3

3 The electron is provided by the grains of acetylene black whereas the H+ proton is provided by <RTI ID=1.9> liteau' of< /RTI> the electrolyte which breaks up into ions OH and H+.

4 A great disadvantage of the pile Leclanché saltworks lies in the fact that the protons are collected by MnO2 but that ions OH are unutilised. It results from it that the pH from <RTI ID=1.10> 1eélectrolyte< /RTI> increases during the discharge of the pile. Calculation shows that the electromotive force of the pile decreases with the pH according to EMI1'S.4 It is true that <RTI ID=2.1> one< /RTI> can partly cure this disadvantage by making intermittent discharges, so that for the periods of rest, the pH reorganizes within <RTI ID=2.2> Itélectrolyte,< /RTI> but such a measurement is insufficient, so that the pile Leclanché saltworks has one relatively limited lifespan.

5 Another disadvantage of the Leclanché element lies in the fact that it is not refillable. In addition, there is a drying of the pile even at relatively low temperatures, which requires to seal it.

6 The present invention relates to a refillable electrochemical generator of greater lifespan and which is less prone to drying. <RTI ID=2.3> Ltinvention< /RTI> is based on the two following ideas - the H+ proton can penetrate in the network of <RTI ID=2.4> MnO 2 there< /RTI> <RTI ID=2.5> +< /RTI> because this last contains water, the H+ proton jumping of a water molecule to following by forming with each one an ion <RTI ID=2.6> H< /RTI> <RTI ID=2.7> O< /RTI> 3 - One should use an electrolyte containing much more protons than the liquid electrolyte used in the pile Leclanché saltworks. The concentrated solutions of acid, such as HCl, are not appropriate since the other electrode of the pile which is out of zinc, risk of corrider.However, it is already known, by many publications, to use acid uranyl phosphate crystallized H U02 P04, 4H20 as an electrolyte. This electrolyte is currently the best known protonic conductive, which is solid at the ordinary temperature, its conductivity being about <RTI ID=2.8> 10< /RTI> <RTI ID=2.9> 3 Q 1< /RTI> <RTI ID=2.10> Cl 1.</RTI>

▲ top

7 The present invention thus relates to a positive electrode for electrochemical generator which is characterized by combination <RTI ID=2.11> of< a /RTI> leaves, of a positive mass made up of an unattackable electronic conducting material, such as the acetylene black of a mixed, electronic and protonic material conducting, such as the manganese oxide <RTI ID=2.12> Mono2< /RTI> of variety Y, and a mineral or organic protonic body solid conducting, and in addition, of an electrolyte consisted a layer of the aforesaid protonic conducting solid body only, two known as layers being taken in mass between them under the effect of the pressure.

8 The aforementioned protonic conducting solid body can <RTI ID=3.1> /RTI< title> consisted <RTI ID=3.2> one< /RTI> of the following mineral acids: - H U02 <RTI ID=3.3> X04< /RTI> nH20, where X is <RTI ID=3.4> one< /RTI> of the elements P, Have..., - H <RTI ID=3.5> M03,< /RTI> nH20 where M is <RTI ID=3.6> one< /RTI> of the elements Sb, Nb, <RTI ID=3.7> Your...</RTI>

9 - H3 (X M12 040,30 H20), where X is <RTI ID=3.8> one< /RTI> of the elements P, Have, and M is one of elements <RTI ID=3.9> Mo,< /RTI> W..., - Zr <RTI ID=3.10> O (H2P04) 2,< /RTI> nH20, - Al203 alumina, H30+ <RTI ID=3.11> pfl< /RTI> or a mixture of these bodies.

10 A preferential example of protonic conducting solid body is the acid uranyl phosphate crystallized H U02 P04, 4H20, that <RTI ID=3.12> one< /RTI> will indicate thereafter by abbreviation HUP.

11 It can also be consisted an organic compound, such as <RTI ID=3.13> Nafion< /RTI> or certain electronic conducting solid polymers.

12 The solid electrolytes, such as HUP are known to be excellent protonic conductive, but nobody before <RTI ID=3.14> n1 had< /RTI> thought of associating them <RTI ID=3.15> MnO 2 there< /RTI> to form an electrode. HUP leads because it contains in its crystallization four water molecules, and that it presents ten sites for hydrogen bonds, nine only being occupied. It is a very concentrated acid (about 8 moles/l).

The protonic property of conduction of HUP arises more when one writes it in the form: U02 <RTI ID=3.16> P04,< /RTI> <RTI ID=3.17> H30< /RTI> 3H20 the H+ proton jumps <RTI ID=3.18> dtune< /RTI> molecule of water to the other.

Conduction is high because the HUP presents a hole which is filled gradually by proton <RTI ID=3.19> but< /RTI> also because it

comprises a uranium atom whose valence is + 6. This atom very strongly retains the two oxygen atoms, so that the connections hydrogen standard with molecules <RTI ID=3.20> /RTI< seal> born not very strong. The proton is thus relatively mobile.

In addition, association HUP - <RTI ID=4.1> klnO 2 there< /RTI> has another advantage: values of the coefficients of diffusion of proton <RTI ID=4.2> H< /RTI> in <RTI ID=4.3> MnO there< /RTI> and in HUP are sufficiently close so that the protons jump <RTI ID=4.4> of< a /RTI> molecule <RTI ID=4.5> doleau< /RTI> of HUP to a water molecule of MnO2- Y without bar <RTI ID=4.6> rière< /RTI> important energetics.

Thus, the invention consists in associating two materials which are known in addition, but that nobody <RTI ID=4.7> nta< /RTI> thought of joining together, fault of having seen that their mode of internal conduction is identical (jump of protons <RTI ID=4.8> of< a /RTI> molecule <RTI ID=4.9> of water< /RTI> with another) and to have highlighted at which point internal water plays an important part in the mechanism of réduc <RTI ID=4.10> tion of MnOz there Y. The unit can thus form /RTI< a positive> electrode of refillable electrochemical generator if one associates it another electrode with lower potential.

Positive mass MnO2- ?, <RTI ID=4.11> MnOOH/HUP< /RTI> - acetylene black also has the advantage of not losing its water molecules contrary to the Leclanché pile in which there is a fast drying of the pile.

The electrode according to the invention can thus be used without any particular protection.

<RTI ID=4.12> Llinvention< /RTI> also relates to a manufactoring process of an electrode which is characterized in that it consists in preparing <RTI ID=4.13> BUP< /RTI> in manner traditional by dissolution of uranyl nitrate crystals in an acid solution <RTI ID=4.14> phosphoriqueà< /RTI> to collect the precipitate of HUP that <RTI ID=4.15> one< /RTI> slack and dries, to also prepare in parallel and in a traditional way a mixture of oxide of manganese and black of acetylene, to mix this last mixture with part of the HUP obtained, in order to form the positive mass, to then separately prepare the electrolyte by putting in a piston the remaining quantity of HUP that <RTI ID=4.16> one< /RTI> packs, to deposit then positive mass <RTI ID=4.17> Nn02/noir< /RTI> of acétylène/HUP formed previously over <RTI ID=4.18> llélectrolyte< /RTI> HUP and to press the two layers so as to cause the catch in mass of <RTI ID=4.19> 1 unit.</RTI>

<RTI ID=4.20> Dcautres< /RTI> advantages and characteristic of <RTI ID=4.21> Itinvention< /RTI> will arise with the reading of the description which will follow, made compared to the annexed drawings in which: Figure 1 is a diagrammatic sight out of cut of an enclosure for <RTI ID=5.1> Itétude< /RTI> of an electrolytic cell using <RTI ID=5.2> 11 /RTI< electrode> according to the invention figure 2 shows the curve of variation of the potential difference according to the time which is imposed during the cyclic voltametry figure 3 is a curve characteristic showing the initial behavior of the pile to course <RTI ID=5.3> of< a cyclic> /RTI voltametry figure 4 shows a curve of discharge <RTI ID=5.4> intensity< /RTI> statics supplements figures 5 and 6 show the evolution of the voltammetric curve during a discharge intensio <RTI ID=5.5> /RTI< statics> figures 7 and 8 show the evolution of the voltammetric curve during a partial intensiostatic refill the electrochemical cell 10 represented on figure 1 is formed by combination <RTI ID=5.6> of< a /RTI> electrolyte 12 out of acid uranyl phosphate crystallized HUP covered on a face with a positive mass 14 consisted a mixture with <RTI ID=5.7> MnO 2 there,< /RTI> HUP and black of acetylene, and on the other face <RTI ID=5.8> of< a /RTI> lay down 16 of platinum.

The preparation of this cell comprises the following operations Préparation of acid uranyl phosphate crystallized <RTI ID=5.9> ? UP:</RTI> HUP can be prepared by the traditional process of precipitation describes since 1848: (cf PASCAL ?New treaty of inorganic chemistry?, Volume XV, 2nd booklet page 483, <RTI ID=5.10> GLASS FRAGMENT< /RTI> ED, Paris 1961), starting from the mixture of nitrate solutions of uranyl and phosphoric acid.

The forks of concentration bringing to the precipitation of HUP were specified by Mr. Dominate-banks (Accounts Returned to the Academy of Science 236, p. 2242-4 (1953): it is necessary that the molecular report/ratio 1/3 and 2. EMI5.1

that is to say included/understood between One lets react during at least 4 hours and <RTI ID=6.1> one< /RTI> obtains a yellow precipitate which is HUP. One extracts water with a water pump, then one spreads out the precipitate and one makes it dry with <RTI ID=6.2> the air< /RTI> during at least 4 hours. After crushing, one obtains a powder usable to prepare the electrolyte and the positive mass.

Preparation of the mixture for the positive mass.

In parallel, one prepares a mixture of <RTI ID=6.3> commercial MnO 2< there> /RTI and of acetylene black, then one mixes the product obtained with part of the powder of <RTI ID=6.4> IIUP< /RTI> prepared previously without crushing <RTI ID=6.5> Itensemble.</RTI> One thus obtains a powder which will be used to form the positive mass or electrode of work of formula: <RTI ID=6.6> MnO2-?< /RTI> , acetylene black, HUP.

One knows that commercial MnO2 of ? variety presents in its network, of the tunnels of large diameter containing of molecules <RTI ID=6.7> of water.</RTI> It is this variety which is used in the Leclanché pile.

<RTI ID=6.8> Enlise in form of cell 10 (figure 1#< /RTI> <RTI ID=6.9> - layer éleetrolyticiue< /RTI> 12.

One pours in a cylinder of piston the remaining quantity of the prepared HUP and one packs it with the piston by applying a moderated force, which gives a body in the shape of disc.

- Layer of <RTI ID=6.10> mixture masses positive-electrolyte< /RTI> <RTI ID=6.11> 14.</RTI>

One places over the disc of HUP which is in the piston, positive mixture <RTI ID=6.12> NnO2-< /RTI> Y, acetylene black, HUP.

One presses the whole until this <RTI ID=6.13> qutil< /RTI> occurs a catch in mass of the two layers. One obtains a rigid pastille in only one part including/understanding a layer 12 of electrolyte HUP of yellow color translucent and a layer 14 of positive mass of color noirâtre (figure 1).

In an example of realization, cell 10 has 13 <RTI ID=6.14> mm< /RTI> in diameter and 1,6 mm thickness; the electrolytic layer 12 be approximately 0,7 mm thickness and contains 300 Mg of HUP; layer <RTI ID=6.15> 14< /RTI> of positive mixture has approximately <RTI ID=6.16> 0,9< /RTI> mm thickness and contain 35,7 Mg of <RTI ID=7.1> En02,< /RTI> 4,3 Mg of acetylene black and 300 Mg of <RTI ID=7.2> XUP.</RTI>

In this example, the force exerted on the piston to carry out the catch in mass is of 10 <RTI ID=7.3> tons/cm2< /RTI> during 1 hour. Similar results can be obtained with other pressures and other durations (for example 1 ton and 8 hours), given that that the larger the exerted pressure is, more duration is short, but <RTI ID=7.4> 1 ' /RTI< thickness> the translucidity and the conductibility of the layers depend on the pressure and the duration.

As shown in the figure 1, the face of the disc of electrolyte 12 opposed to that which carries the positive mass is covered <RTI

ID=7.5> of< a /RTI> sleep of platinum 16 deposited starting from a dried lacquer then a few hours. This layer of platinum is used as counter-electrode.

One will study now some experimental results obtained with such a cell 10.

Cell 10 is introduced inside <RTI ID=7.6> dtune< /RTI> enclosure 18 container an atmosphere of hydrogen saturated with steam to the atmospheric pressure. It is posed on a metal support 20 which is connected electrically to <RTI ID=7.7> /RTI< negative> pole of a source of D.C. current.

The positive mass 14 and counter-electrode 16 are in contact with the hydrogen saturated with vapor <RTI ID=7.8> of water.</RTI> the contacts are ensured by pressure on a metal cylinder 22 which takes support on the positive mass and which receives the push of a metal stem 24 connected to <RTI ID=7.9> /RTI< positive> pole of the power source, a metal spring 26 being interposed between the stem 24 and the cylinder 22.

It will be noted that one could put only counter-electrode 16 in contact with the hydrogen saturated with steam.

It is essential to use vapor <RTI ID=7.10> of water< /RTI> bus in its absence the hydrogen electrode could not function.

The experimental method of study of the electrolytic cell 10 is carried out in the following way: The cell is discharged <RTI ID=8.1> intensiostatiquement,< /RTI> i.e. with constant intensity, <RTI ID=8.2> # ino 2 there< /RTI> playing the part of cathode then and transforming themselves into <RTI ID=8.3> NnOOH,< /RTI> then is reloaded intensiostatiquement, <RTI ID=8.4> #1nOOH< /RTI> playing the part of anode and retransformant themselves in <RTI ID=8.5> Be 2*< /RTI> In the example selected, the discharge was made with a constant intensity of 0,5 my, but this value is not restrictive. <RTI ID=8.6> the /RTI< electrode> according to <RTI ID=8.7> the /RTI< invention> makes it possible to support intensities considerably higher.

During discharges and refills, the current is several times crossed in order to be able to each time make a triangular voltametry by cycling of the potential difference U at the boundaries of the cell, around the value of Uo abandonment after cut of the current.

It is pointed out that a cyclic triangular voltametry consists in raising the curve I = F (E) of current I according to the potential E of the electrode of work when one <RTI ID=8.8> fact of varying this potential around the value of abandonment E O< /RTI> This variation is carried out by means of a generator of signals in teeth of saw and <RTI ID=8.9> of< a /RTI> potentiostat, which explains triangular name voltametry.

In this case, it was supposed that the contreélectrode 16 with hydrogen was impolarizable for this zone of densities of current and that consequently the variations of U at the boundaries were those of the potential of positive mass <RTI ID=8.10> MnO there< /RTI> HUP.

Tests were carried out with a potential difference whose curve of variation with time is represented on figure 2. The potential difference varies between + 175 mV with a speed of 50 <RTI ID=8.11> mVs#1.</RTI>

Each sweeping begin with an increase from the potential difference at the boundaries of the cell.

Experimental results initial State of the cell After its manufacture, cell 10 is placed in enclosure 18 and one observes that its electromotive force believes regularly until reaching in a few seconds a stable value <RTI ID=9.1> Eo< /RTI> = 1,263 volt.

A cyclic voltametry is then made on a score of cycles in the interval of potential difference 1,1 - 1,4 volt (or more exactly 1,088 1,438 volt).

The curve I = F (U) obtained is represented on figure 3. With the first cycle, the intensity varies according to curve <RTI ID=9.2> Al</RTI> One notes that curve A obtained for the twentieth cycle is practically identical to that of the first cycle, which proves that the electrode according to the invention is reversible with transformation, i.e. the cycle reproduces with transformation in the positive electrode of MnO2 into MnOOH and conversely.

<RTI ID=9.3> Lsshystérésis< /RTI> that <RTI ID=9.4> Iton< /RTI> notices on the cycles is due precisely to <RTI ID=9.5> Itoxydo /RTI< reduction> which RTI <ID=9 undergoes.6> Mono2< /RTI> which passes from <RTI ID=9.7> mn (+iii)< /RTI> with <RTI ID=9.8> mn (+IV) and< /RTI> conversely.

Complete discharge of the cell.

The discharge is made with constant intensity equalizes 0,5 my. The complete discharge lasts 17 hours (figure 4).

It is noted that the potential difference at the boundaries of the cell presents a stage around U = 1,1 volt which lasts approximately 10 hours. It is an important advantage of the cell according to the invention compared to the pile Leclanché saltworks which does not comprise a stage.

It is interesting to know that with the intensity chosen, the output of <RTI ID=9.9> Itélectrode< /RTI> positive is higher than 80%, and that the initial ohmic fall is 26 mV, and of 120 mV to U = 0,2 V.

Evolution of curve <RTI ID=9.10> voltanimetric< /RTI> during a discharge <RTI ID=9.11> intensiostatîgue.</RTI>

During the complete discharge, one stops several times the current, for example at the points A, B, C and D of curve 5, where the potential difference is respectively 1,263; 1,1; 1,0 and 0,9 volt. For each one of these values, the cell is left with <RTI ID=9.12> the abanv4.one< /RTI> during 3 minutes, which makes it possible the electromotive force to be stabilized, then one carries out a cyclic voltametry, as one described in connection with figures 2 and 3.

On figure 6, one represented curves <RTI ID=10.1> voitammetric< /RTI> corresponding to points A, B, <RTI ID=10.2>< /RTI> and D of the curve of discharge of figure 5. Curve A is, of course, that of figure 3 and corresponds at the initial state of the cell.

It is noted on the one hand, that each one of these curves does not evolve/move during successive cycles, and on the other hand, that the slope of the curves decreases as the tension of cut decreases.

Evolution of curve <RTI ID=10.3> voltammétriclue< /RTI> with the course a refill <RTI ID=10.4> intensiostatipue< /RTI> partial.

After the point of discharge D (figures 5 and 6), one reloads the cell; during this refill one stops 2 times the current with the tensions of cut 1,210 V (points E and F) and 1,310 (not G). The points E and F correspond to two durations different of abandonment. Figure 7 thus is obtained.

As previously, one carries out for each one of these values of cut, a cyclic voltametry, which gives curves D, E, F and <RTI ID=10.5> G shown< /RTI> on figure 8.

As during the phase of discharge, the voltammetric curves do not evolve/move during successive cycles. It is still noted that the slope of the aforesaid curves does not vary.

Analyze results obtained.

The whole of voltammetric curves obtained <RTI ID=10.6> watch that the two couples MnO2- Y, binOOH/HUP (positive< /RTI> mass) and HUP/Pt, H2, vapor H20 (electrolyte) are reversible and stable in the cell.

The following observations can be made on the voltammetric curves of figures 6 and 8.

- slope <RTI ID=10.7> y< /RTI> are very high in <RTI ID=10.8> the initial< state> /RTI <RTI ID=10.9> E of the cell and after a discharge arratée with< a /RTI> potential difference 1,1 volt. It results from it that mass <RTI ID=11.1> mn 02 there,< /RTI> MnOOH/HUP is reversible and stable.

- this slope is weaker but remains nevertheless stable and practically constant for major discharges and after the refills.

- in the same way that for the slope, lthystérésis observed on the voltammetric curves, weak lement initiated (curved A and B), becomes more important for a potential difference of discharge lower than 1,1 volt, but remains appreciably the same one during later handling of discharge and refill (curves C with G).

- positive mass <RTI ID=11.2> MnO2 -< /RTI> Y, MnOOH/HUP probably undergoes an irreversible transformation into lower part of a potential difference of discharge of 1,1 volt and the new system is <RTI ID=11.3> him-m8me< reversible> , stable and refillable /RTI.